First Principles Calculation of 2-Dimensional Silicides Formed on Nickel Surfaces

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Metal silicides are indispensable materials for advanced microelectronics. We have recently proposed a new route to form a robust two-dimensional (2-D) silicide [1,2]. Unlike conventional thin film silicide formed by depositing metal on the silicon surface, Si was deposited on a clean metal surface to form silicide. Our recent studies show that robust 2-D silicides are formed on Ni(110) and Ni(100) surfaces due to the large diffusion asymmetry between Si in bulk metal and metals in bulk Si [1,2]. However, the lack of theoretical support clearly undermines the significance of our research findings.

First-principles calculation code VASP was adopted to compare the experimentally obtained 2-D atomic structure with theoretical simulations. A typical scanning tunneling microscope (STM) image of a Si-deposited Ni(100) surface is shown in Fig. 1 [2]. The initial clean surface was essentially a 1×1 structure, but many dark sites were formed after Si deposition. These dark sites are not due to structural defects, but Si replaced by Ni in the top layer. Since the STM image is reflected by the surface local density of states (LDOS) near E_F, the embedded Si reduces the tunneling current without the large LDOS due to Ni 3*d* bands, making it a dark site. Therefore, the discrimination between individual Si and Ni is fairly straightforward, but the relationship between Si and Ni is unsolved.

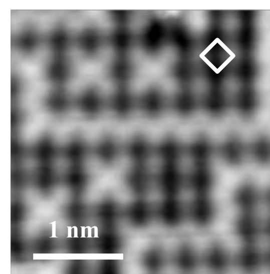

Fig. 1 Typical STM image for a 0.39 ML Si deposited surface. White square corresponds to the 1×1 unit cell.

Therefore, the first principle calculation was performed in this system. The calculation parameters are shown in Table 1. Before performing surface slab calculations, we evaluated the ground state energies of Ni and Si atoms, and bulk Ni and Si, respectively. Because of the slow convergence of self-consistent electronic states in the surface structure, we adjusted the mixing parameters as

shown in Table 1 (so-called linear mixing, see VASP manual). First, all atoms except for the middle layer has been completely relaxed. Then 0-8 surface Ni atoms in the top layer were replaced by Si, and the top 5 layers were fully optimized. A total of 36 different surface configurations were evaluated for 0-1 ML Si coverage.

In order to compare the formation energy for different numbers of surface species, we evaluated chemical potential as,

$$E_{total} = E_{slab} - n_{Ni}E_b^{Ni} - n_{Si}E_b^{Si},$$

where E_{slab} is a total energy of a particular slab structure, n_{Ni} and n_{Si} are respectively numbers of Ni and Si atoms in the slab, and E_b^{Ni} and E_b^{Si} are respectively bulk cohesive energies for Ni and Si.

As shown in Fig. 2, the relative energies of various configurations referenced from that for the Ni(100) surface are plotted as a function of Si coverage. Negative formation energy means that energies of Si embedded structures are lower than that of the Ni(100). There is a negative slope for Si coverage from 0 to 0.5 ML, indicating that Si substitution with Ni is energetically favorable. On the other hand, a positive slope above 0.5 ML means that Si will be ejected from the structure, which is in good agreement with experimental observations.

In conclusion, the first-principles study of two-dimensional Ni silicide formed on Ni (100) is in good agreement with the experimental results. As a future study, the displacement process, so-called depressive adsorption, should be revealed by molecular dynamics simulations.

Table 1 Parameters for present calculation

VASP Version	5.3.5
slab geometry	Ni(100) 2×4 unit 11 layers
vacuum region	2.12 nm
k-points	16×8×1
potential	PBE [3]
cut off energy	350.39 eV
Fermi level smearing	Methfessel & Paxton σ = 0.12 eV
convergent condition ion cordination electronic states	 0.01 eV/Ang. 10^{-5} eV
mixing parameters	spin-resolved AMI = 0.02 BMIX = 0.0001 AMIX_MAG = 0.08 BMIX_MAG = 0.0001

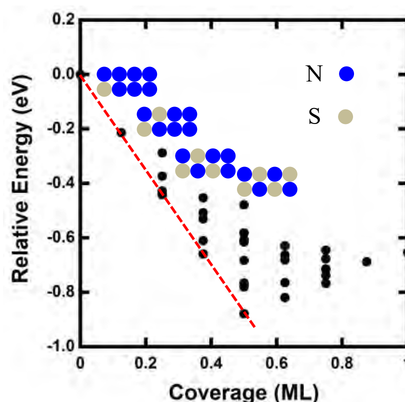

Fig. 2 Relative formation energies of Si-embedded Ni(100) surfaces with various configurations of Si coverage between 0-1 ML. Inset: The most stable configurations with Si coverage of 0.125, 0.25, 0.375, and 0.5 ML.

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